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A NEW RESEARCH TOOL

THE DIFFERENTIAL THERMOBALANCE

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The differential thermobalance

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SUMMARY.   The author has devised a new method of thermo-gravimetric analysis which instead of recording the total loss of weight of a sample of temperature $p = f(t)$ establishes the differential curves
$$\frac{dp}{dt} = f'(t).$$

The precision of the recording on a relatively small scale is equal to that which would be given by the integral curve traced on a very large scale.

The curves obtained have the same appearance as those of differential thermal analysis, but have the advantage over the latter of having quantitative values.

The author describes an automatic apparatus which allows the direct establishment of the thermo-gravimetric differential curves.

In a recent book, Clement Duval (1)[*] has demonstrated the great interest which can be taken in what he called thermo-gravimetric analysis.

There are numerous models of thermobalances for carrying out this analysis. These instruments make it possible to measure or record the loss of weight of a sample placed in a furnace.

The loss of weight can be recorded as a function of the time at constant temperature or may be measured for a gradual elevation of the oven temperature.

Numerous arrangements have been devised and we have described the one developed by us when working on Belgian clays. (2)

Thermo gravimetric analysis may be compared to thermal analysis whenever the phenomenon caused by elevation of temperature is accompanied by loss in weight.

It is particularly useful and interesting in the study of the decomposition of hydrates and carbonates.

It has the advantage over thermal analysis of having more value quantitatively. Actually, if the decomposition temperature of a hydrate, a hydrated silicate or a carbonate is known, the loss of weight at this temperature allows the determination of the weight of the hydrate or the carbonate contained in the substance analysed.

It was with this aim in view that some years ago we made great use of the thermobalance in the study of clay substances. (2)

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[*] For references see end

We tried at that time to record photographically, but we abandoned the attempt as we were unable to obtain a large scale diagram in a simple enough manner, and under these conditions one is forced to use a balance of low sensitivity or to use very small quantities of material. In both cases precision suffers a great deal.

Further, when a slight loss of weight takes place at a temperature slightly higher than that of an appreciable loss of weight, the second phenomenon is not always distinguished, and for this reason we were held to the tedious method of weighing at intervals of one minute.

In this way it was possible in spite of convection currents in the furnace and without the latter having any effect on the weights, to make these weighings within a milligram, the sample in the furnace weighing 2.5 grams. In this way we obtained fairly accurate diagrams.

Under these conditions, the principal loss of weight of a clay taking place corresponded to a recording dimension of 300 mm. The inconvenience of graphical representation of this type consists in producing diagrams which are certainly accurate, but of very large dimensions, of which the printed reproduction is practically impossible.

On the other hand, even when working with a very large sample, it is sometimes difficult to solve the problem of the determination of the commencement of dehydration of a hydrate whose decomposition temperature is fairly close to that of another hydrate.

In order to determine such temperatures a change was made to graphic differentiation of the weight loss curves.

Henceforth, the total loss of weight is no longer represented by the difference between the initial and final ordinates, but at the area lying between the differential curve and the abscissa.

The result is that without sacrificing accuracy, one can obtain a diagram of much smaller dimensions.

On the other hand, the indication of the commencement of dehydration is much more precise than for the cumulative initial curve.

Thus curve II in figure I represents the differential curve of loss of weight of a sample of Zettlitz kaolin to which 10% of diaspore is added.

We are able to distinguish clearly between the beginning of dehydration of the Zettlitz kaolin T, and the beginning of dehydration of the diaspore T_2.

Such a distinction is hardly possible on the initial diagrams, even when these are drawn on a very large scale.

The differential diagrams obtained in this way have the additional interest of being directly comparable to those obtained by differential thermal analysis. In the case where the phenomena are due solely to loss of weight, these diagrams are practically identical.

The result is that the comparison of the differential diagrams obtained by one method or the other allows us to distinguish between reactions accompanied by losses of weight and those which take place at constant weight.

Differential thermal analysis having become a simple matter thanks to the various automatic instruments which are adapted to it, we have devised an automatic differential thermo-gravimetric apparatus.

The principle of the apparatus is based on the fact that when the graphical differentiation of the curve loss of weight/temperature is made, we take as ordinate the difference of weight of the sample between temperature t and temperature t + dt, dt being constant whilst t varies gradually with the raising of the temperature of the oven.

We were able to obtain the curve dp/dt directly by using the apparatus described below (Figure 2).

This apparatus consists essentially of two cylindrical electric furnaces of identical construction and sufficiently accurately matched.

On the balance pans are placed two crucibles of equal size containing exactly the same amount of material to be studied.

These furnaces are gradually heated from room temperature to a temperature higher than that at which the losses of weight under investigation take place.

An electrical device allows us to maintain one of the two furnaces at a temperature slightly below that of the other.

A device suitable for this effect consists of a variable resistance placed in series with one of the two furnaces.

In this way, the deviation of the balance beam is proportional at each temperature to the difference in weight between the two crucibles.

Since the phenomena attendant on the elevation of temperature (the losses in weight) are the same in the two crucibles for equal quantities of the substance, the deviation of the beam is proportional to the difference of weight of the substance at temperature t and temperature t + dt, dt being the constant difference of temperature between the two furnaces.

By fixing a mirror on the balance beam we were able by means of a suitable optical arrangement, to record the displacement of a luminous spot, this displacement being a function of the difference in weight between the two samples.

This luminous spot falls on photographic paper rolled on a drum turning at constant velocity. In this way images similar to curve II in figure 1 are obtained.

The abscissa of this curve is the time, and if the elevation of the temperature is regular, it is proportional to the temperature.

Under these conditions, the curves obtained are really the curves

$$\frac{dp}{dt} = f\,(t)$$

Figures 3 and 4 represent differential thermo-gravimetric curves obtained by means of the apparatus discribed above and we have shown for comparison the curves obtained by differential thermal analysis.

As we said above, it is possible by means of these curves, to evaluate fairly precisely losses of weight corresponding to various phenomena.

If heating is carried out to 1000°, it is possible by simple calcination at 1000° to determine the total % loss of weight.

On the differential diagram, this loss of weight is represented by the total area between the curve and the abscissa, each individual loss of weight being determined on the same scale by the area between the section corresponding to the phenomenon under consideration and the abscissa.

Thus the loss of weight corresponding to the loss of humidity of Zettlitz kaolin will be represented by the area S_1 (fig. 3) and that due to the dehydration of the kaolinite, by the area S_2.

In the same way for the magnesium carbonate (fig. 4) the area S_1 represents the humidity. The area S_2 the water of crystallisation of the basic carbonate.
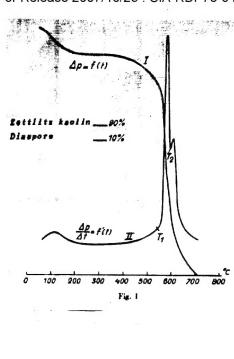
Measurement of these areas will allow the determination the content in the substance of each of its hydrated or carbonated constituents.
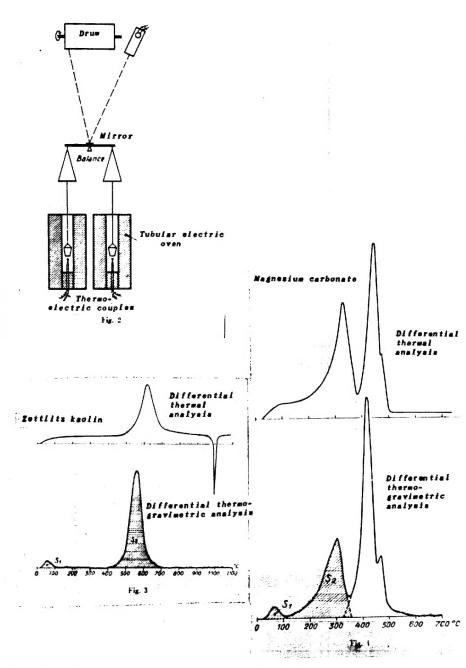
REFERENCES

(1) Inorganic thermo-gravimetric analysis, Elsevier 1953.

(2) Annales des Mines de Belgique, 1938-1939,
      Chap. VI, p. 257.

$\Delta p = f(t)$ I

Zettlitz kaolin ___ 90%
Diaspore   ___ 10%

$\frac{\Delta p}{\Delta t} = f(t)$ II T_1

T_2

Fig. 1

Drum

Mirror

Balance

Tubular electric oven

Thermo-electric couples

Fig. 2

Zettlitz kaolin

Differential thermal analysis

Differential thermo-gravimetric analysis

Fig. 3

Magnesium carbonate

Differential thermal analysis

Differential thermo-gravimetric analysis